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Inhomogeneity in the molecular structure of cellulose nitrates

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Abstract. The results of studies on the molecular structures of cellulose nitrates and related saccharide nitrates are surveyed. The inhomogeneity of the structures of cellulose nitrates can be analysed on three hierarchical levels: in terms of the composition of the elementary units, in terms of the distribution of the elementary units along the chain, and in terms of their distribution in the bulk phase. The possibilities of the NMR and FT-IR spectroscopy for studies of these structural levels are discussed. A simple method has been developed for the estimation of the molecular-structural inhomogeneity of cellulose nitrates. It is shown that this inhomogeneity is determined by the inhomogeneity of the nitration process. A procedure is proposed for taking into account the diffusion of the nitrating agent in studies of the kinetics of the inhomogeneous reactions. The bibliography includes 121 references.

I. Introduction

Cellulose nitrates (CN) are polymers the production of which always took place long before studies of their structural characteristics. For this reason, the technology of the preparation of cellu-lose nitrates has been largely based on empirical rules and has been developed by the method of trial and error. Despite the large scale production of cellulose nitrates for gunpowders, rocket fuels, varnishes, dyes, biological membranes, ionising radiation detectors, etc., the characteristics of their molecular structure, as manifested in the properties of these polymers, have not so far been investigated: the structure – property correlations have not been found. There are comparatively few surveys of studies on the structure of cellulose nitrates.[1–14] However, recently studies on the detailed molecular structure of cellulose nitrates have received a fresh stimulus from the development of molecular spectroscopic methods yielding data with a high information content — high-resolution ^{13}C and ^{15}N NMR and FT-IR spectroscopy.

The present review is devoted mainly to studies on the molecular structure of cellulose nitrates and on their structural inhomogeneity.

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II. Molecular structure of cellulose nitrates

Cellulose nitrates constitute a family of incompletely substituted cellulose esters having the general formula $-[-C_6H_7O_2.(ONO_2)_x(OH)_{3-x}-]_n-$, where $0 < x \leqslant 3$. Cellulose nitrates with different values of x have different properties, the most important of which are solubility and plasticisability. The principal feature of cellulose nitrates is their heterounit structure. In the general case, cellulose nitrate chains include eight types of elementary unit: one unsubstituted glucopyranose ring; three monosubstituted (2-, 3-, and 6-monosubstituted) pyranose rings; three disubstituted (2,3-, 2,6-, and 3,6-disubstituted) pyranose rings; and one 2,3,6-trisubstituted pyranose ring (Fig. 1).

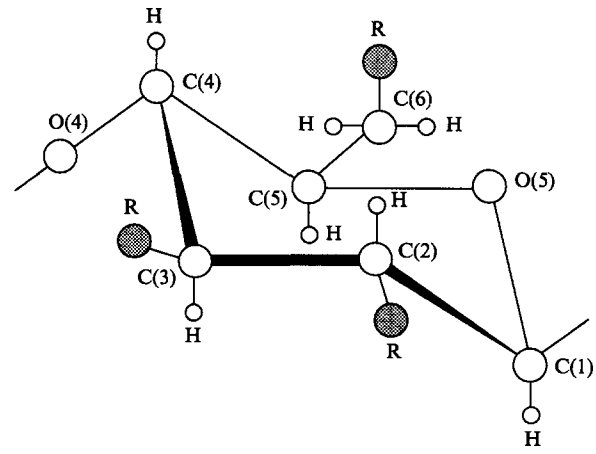


Figure 1. The numbering of the atoms in the elementary unit of cellulose nitrate. R = —OH or $-ONO_2$.

1. Conformation of the cellulose nitrate macromolecule

Like the majority of crystalline polymers, cellulose nitrates give rise to a diffraction pattern with a small number of reflections, from which it is difficult to obtain complete information about the conformation of the cellulose nitrate chains. The unit cell parameters of cellulose nitrates (with a nearly limiting degree of substitution) have been found.[1,15–17] The parameters of the orthorhombic unit cell found by different workers agreee fairly closely, which makes it possible to regard them as reliable (Table 1).

Table 1. The unit cell parameters of cellulose nitrate.

Degree of substitution	a/nm	b/nm	c(IP)/nm[a]	Ref.
2.8	0.90	1.39	2.56	1
2.8			2.57	15
2.8	0.855	1.230	2.54	16
2.9	0.90	1.224	2.54	17
2.9	0.90	1.46	2.54	17

[a] The parameter c corresponds to the identity period.

The identity period (IP) of 2.54 nm and the corresponding meridianal reflections on the diffraction patterns of cellulose trinitrates (CTN) indicate directly that the cellulose nitrate chains are packed in the form of a 5_2 helix (five elementary units for two turns of the helix). Cellulose has IP = 10.3 Å, which corresponds to a 2_1 helix (a planar zig-zag conformation with two units per identity period).[18]

Consequently the appearance of bulky nitrate substituents on passing from cellulose to CTN is accompanied by the uncoiling of the macromolecular helix (the twist angle of the helix varies from 180° for cellulose to 144° for cellulose nitrate). The question of the parallel or antiparallel arrangement of the chains in crystalline cellulose nitrates has so far remained open.[17] We are aware of only one study[19] in which the most favourable conformations of isolated chains of CTN and cellulose di- and mono-nitrates were calculated by the method of molecular mechanics. Structural models, consistent with experimental data and corresponding to the deepest minima on the potential energy surface for the macromolecules, were constructed. A chain conformation close to 2_1 obtains for cellulose mononitrates, which probably reflects the smaller 'saturation' of the polymer skeleton by nitrate groups compared with CTN. Conformational states of the chains ranging from the 2_1 helix to the 5_2 helix, depending on the degree of substitution of the cellulose nitrates, are probably possible for cellulose nitrates with degrees of substitution less than three.

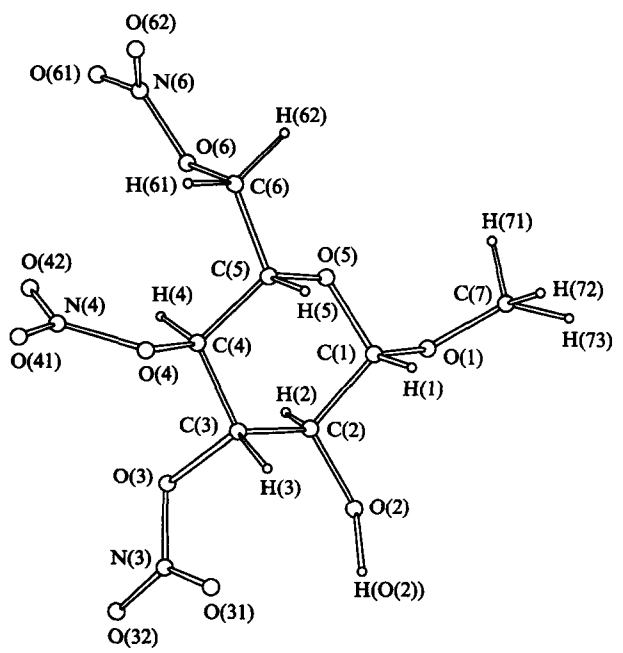


Figure 2. The geometry of the molecule of the 3,4,6-trinitrate of methyl β-D-glucopyranoside.[26]

2. Conformation of the glucopyranose ring

Unfortunately there are no direct experimental data concerning the conformation of the pyranose ring in cellulose nitrates. It has been demonstrated in a review[18] that the glucopyranose ring in cellulose and model saccharides[20] has the $^4C_1$ (chair) conformation with an equatorial disposition of the substituents. The ring conformations in the cellulose nitrate chain have been calculated by the method of molecular mechanics and it has been shown that the $^4C_1$ chair conformation is the most favourable.[11,21,22] A series of studies on the X-ray diffraction of model glucoside and cellobioside nitrates have been published recently.[23–29] They were concerned with the 2,3-dinitrates of methyl 4,6-*O*-ethylidene-β-D-glucopyranoside (2,3-DNMEG) (the α- and β-anomers), the 3,6-dinitrate of methyl 4-*O*-methyl-β-D-glucopyranoside (3,6-DNMMG), the 2,4,6- and 3,4,6-trinitrates of methyl β-D-glucopyranoside (2,4,6- and 3,4,6-TNMG) (Fig. 2), the 2,3,4,6-tetranitrate of methyl β-D-glucopyranoside (2,3,4,6-TNMG) (Fig. 3), and the 6,6′-dinitrate and the 2,3,6,2′,3′,4′,6′-heptanitrate of methyl β-D-cellobioside (6,6′-DNMC and 2,3,6,2′,3′,4′,6′-HNMC) (Figs 4 and 5).

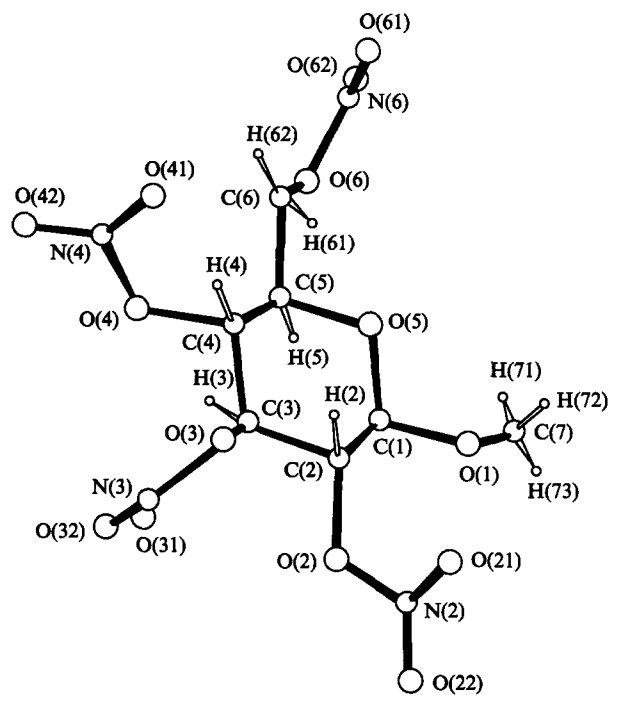


Figure 3. The geometry of the molecule of the 2,3,4,6-tetranitrate of methyl β-D-glucopyranoside.[27]

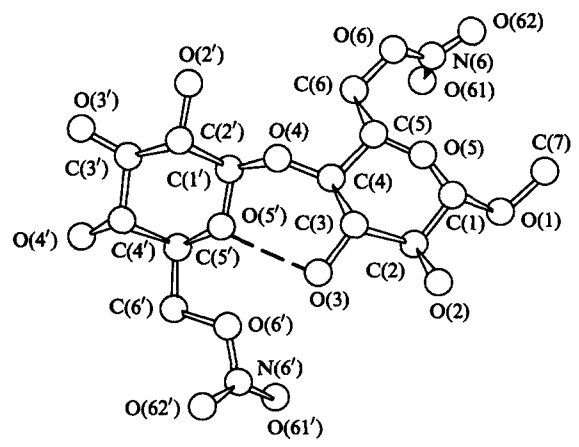


Figure 4. The geometry of the molecule of the 6,6′-dinitrate of methyl β-D-cellobioside.[28]

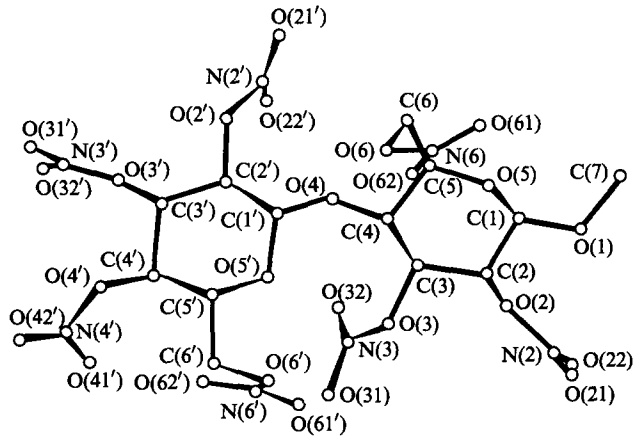


Figure 5. The geometry of the molecule of the 2,3,6,2',3',4',6'-heptanitrate of methyl β-D-cellobioside.[29]

Without exception, they all have the $^4C_1$ conformation of the glucopyranose ring regardless of the number of substituting nitrate groups or the presence of the second ring in 2,3-DNMEG.

Thus it is evident that the conformation of the glucopyranose ring is fairly stable. One must recall that, in an attempt to describe the conformation of the CTN chain, Watanabe and coworkers[15,30] used the 'half-boat' conformation, assuming erroneously that the conformation of the nitrate groups along the cellulose nitrate chain is more 'rigid' than the conformation of the pyranose rings. The 'half-boat' conformation has also been used for the description of the model of the folded chain of cellulose II.[31] However, later studies demonstrated that this model conflicts with the concept underlying the biosynthesis of cellulose.[9]

3. Conformations of the nitrate groups

Calculations for cellulose and cellobiose nitrates[32] as well as for fragments of the CTN chains,[11,21,22] carried out by methods of molecular mechanics, have shown that a large number of stable conformers are possible for the nitrate group in the C(6) position†. This is evidently determined by the presence of two conformational degrees of freedom — the internal rotations relative to the C(5)–C(6) and C(6)–O(6) single bonds. X-Ray diffraction studies on model saccharide nitrates confirm the results of the calculations: different C(4)C(5)C(6)O(6) and C(5)C(6)O(6)N(6) torsional angles for the given fragment are observed in the crystal (Table 2).

The nitrate groups in all the compounds investigated are planar. The internal rotation of the nitrate groups in cellulose nitrates in the 2- and 3-positions takes place relative to the C(2)–O(2) and C(3)–O(3) bonds [C(1)C(2)O(2)N(2) and C(2)C(3)O(3)N(3) torsional angles]. However, their close proximity limits their mutual orientation. These groups have different locations relative to the pyranose ring. The results of calculations have shown that both groups 'tend' to achieve a mutually perpendicular disposition.[32] According to X-ray diffraction data, the angles between the planes of the nitrate groups, for example in 2,3-DNMEG,[23] are 82° for the α-anomer and 76° for the β-anomer, whereas in 2,3,4,6-TNMG the angle is 75°.[27] The $-CONO_2$ groups are significantly nonplanar. The maximum displacement of the carbon atom from the plane of the nitrate group reaches 23° for 2,3-DNMEG and 21° for 2,3,6,2',3',4',6'-HNMC.

In conclusion of this section, we emphasise that its main aim was not so much the discussion of controversial problems concerning the conformational state of cellulose nitrates as the description of the most important and reliable parameters necessary for the consideration of the molecular-structural inhomogeneity of cellulose nitrates. Readers who are interested may obtain the necessary details from the literature sources quoted.

† The term 'conformer' is understood as the mutual disposition of atoms in the molecule or its fragment which corresponds to global or local energy minima, whilst the term 'conformation' implies any kind of their mutual disposition.[81]

Table 2. The torsional angles (deg) in the molecules of the monosaccharide and disaccharide nitrate single crystals.

Angle	2,3-DNMEG[a]	3,6-DNMMG	2,4,6-TNMG	3,4,6-TNMG	2,3,4,6-TNMG	6,6'-DNMC[b]	2,3,6,2',3',4',6'-HNMC[b]
C(1)C(2)O(2)N(2)	−80.5 / 88.4	–	122.3	–	97	–	95.3 / 95.4
C(2)O(2)N(2)O(21)	19.5 / −156.4	–	−177.3	–	−163.5	–	1.8 / −158.5
C(2)C(3)O(3)N(3)	104.7 / 99.0	−117.4	–	−97.5	−120	–	−130.9 / −146.8
C(3)O(3)N(3)O(31)	174.4 / 172.8	−0.5	–	−17.2	−6.1	–	177.5 / 178.5
C(3)C(4)O(4)N(4)	–	–	134.9	127.9	not quoted	–	– / 136.8
C(4)O(4)N(4)O(41)	–	–	−170.1	−175.8	−5.5	–	– / 5.8
C(4)C(5)C(6)O(6)	−57.6 / −56.8	53.3	59.2	60.4	not quoted	−176.7 / −178.4	42.5 / −179.1
C(5)C(6)O(6)N(6)	–	−178.0	−162.7	−169.1	not quoted	−95.7 / −23.0	101.4 / 93.7
C(6)O(6)N(6)O(61)	–	−2.0	179.8	177.1	−169.5	−171.5 / −174.5	−2.7 / −178.6

[a] Numerator — α-anomer, denominator — β-anomer.
[b] Numerator — first pyranose ring, denominator — second pyranose ring.

III. High-resolution NMR studies on the molecular structure of cellulose nitrates

The development of the experimental NMR technique has significantly expanded the scope of studies on the detailed molecular structure of cellulose nitrates. Interesting results have been obtained with the aid of high-resolution ^{13}C NMR spectroscopy in solution.[33-44] At the beginning of the 1980s, two publications appeared independently on the analysis of the NMR spectra of cellulose nitrates and their analogues,[33,34] in which the ^{13}C NMR spectra of cellulose nitrates were interpreted for the first time. Wu[33] showed that, with the aid of NMR, it is possible not only to distinguish the signals of the carbon atoms sensitive to the location of the nitrate groups but also to determine the ratio of the types to units with different numbers of nitrate groups. A rigorous interpretation of the NMR spectra of cellulose nitrates has now been achieved based on numerous studies of the NMR spectra of model nitrates[34,39,43] and specially synthesised cellulose nitrates,[33,35,36,41] as well as on calculations of the chemical shifts of the nuclei from their increments[41,44] (Table 3).

Cellobiose octanitrate (CON) is the closest structural analogue of CTN. In CON, it is possible to differentiate a molecular fragment (Fig. 6) which gives rise to NMR signals least perturbed by the terminal sections of the molecules which are not similar to those in the CTN. Analysis of the chemical shifts of the nuclei (Table 3) showed that the positions of these particular signals in the spectra are closest to the positions of the CTN signals. It has been suggested that the neighbouring elementary units exert a significant influence on the chemical shifts of the nuclei of the glucoside ring.[34,36] Together with this, it is also necessary to take into account the conformational state of the chains and substituents in cellulose nitrates. The 10% solutions of cellulose nitrates employed in the NMR experiments are very different from the equilibrium solutions, in which there is no interchain interaction and homogeneous conformations of the macromolecules are achieved.[9] In this case, the differences between the chemical shifts of CON and CTN under identical experimental conditions may be accounted for by the following factors: (1) the inadequacy of the model (Fig. 6), (2) the more extensive conformational set of the CTN chains, (3) the influence of neighbouring units on one another, and (4) the heterounit structure in the case of cellulose nitrates with a degree of substitution less than 3. The differences between the positions of the signals of the tetranitrate of methyl glucoside, cellobiose octanitrate, and CTN hardly exceed 1 ppm (Table 3). This is evidence indicating that the mutual influence of the units in cellulose nitrates is insignificant (for example, a change of solvent leads to similar differences between the chemical shifts and one may expect that different solvents may ultimately act specifically on the conformations of the cellulose nitrate chains). Consequently the parameters which influence significantly the magnitudes of the chemical shifts of cellulose nitrates are the heterounit structure of the polymer and the differences between

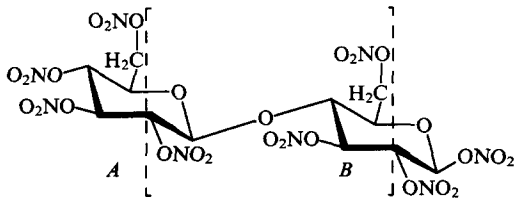


Figure 6. The structural formula of cellobiose octanitrate. The molecular fragment modelling CTN is shown in square brackets.

the conformational states of the cellulose nitrate chains. An important conclusion which follows from the analysis of the data in Table 3 is that the NMR spectrum actually corresponds to a single elementary unit of CTN; the influence of the neighbouring units (at least for the modern apparatus with a resolution corresponding to 100 MHz) is negligible.

The ^{13}C NMR spectrum of a cellulose nitrate specimen with a degree of substitution of 1.2 in solution in DMSO shows clearly (Fig. 7) that the main group of lines is concentrated in the region of 70-90 ppm where the signals of different nuclei overlap. The most remote and nonoverlapping region, 95-105 ppm, belongs to the signals from the C(1) atoms. By analysing carefully the chemical shifts for selectively substituted nitrates of methyl glucosides and cellulose nitrates with different degrees of substitution (Table 4), it is possible to separate reliably the signals obtained from different elementary units of cellulose nitrates.

Table 4. The chemical shifts (ppm) for the resonances of the C(1) carbon atom in the nitrates of methyl β-D-glucosides (NMG) and in cellulose nitrate.

Positions of nitrate groups	NMG[39]	CN[41]	CN[44]
2	101.6	99.7	(99.0)
2,3	101.6	(100.9)	(98.6)
2,4	101.4	–	–
2,6	101.4	98.8	(97.3)
2,3,6	101.6	100.0	(98.3)
2,4,6	101.35	–	–
2,3,4,6	101.4	–	–
Unsubstituted unit	104.8	104.4	(103.1)
6	104.85	103.5	(102.8)
3	104.3	(106.1)	(102.4)
3,6	104.95	105.2	(103.0)
3,4,6	104.45		

Note. The chemical shifts calculated from the increments are given in brackets.

Table 3. The chemical shifts (δ/ppm) of the 2,3,4,6-tetranitrate of methyl β-D-glucoside, β-cellobiose octanitrate, and cellulose trinitrates.

Atom	δ(2,3,4,6-TNMG) according to data in Refs		δ(CON-*A*) according to data in Refs		δ(CON-*B*) according to data in Refs		δ(CTN) according to data in Refs		
	39	43	34	43	34	43	34	43	41
C(1)	101.4	101.35	100.1	100.26	96.1	96.64	100.1	100.14	100.0
C(2)	79.1	79.06	78.5	78.58	74.8	74.73	78.3	79.28	80.6
C(3)	78.8	79.06	78.6	78.58	79.0	78.96	79.4	78.06	79.5
C(4)	76.9	76.88	76.0	75.94	76.75	77.02	76.8	77.02	77.2
C(5)	70.35	70.30	69.8	69.66	72.6	72.50	71.7	71.37	71.9
C(6)	71.1	71.12	70.5	70.65	70.1	70.23	70.6	70.72	71.9

Note. Here and henceforth the chemical shifts corresponding to those of CTN are underlined (Fig. 6). The last column presents data for a solution of CTN in dimethyl sulfoxide, while the remaining columns present data for solutions in acetone-d_6.

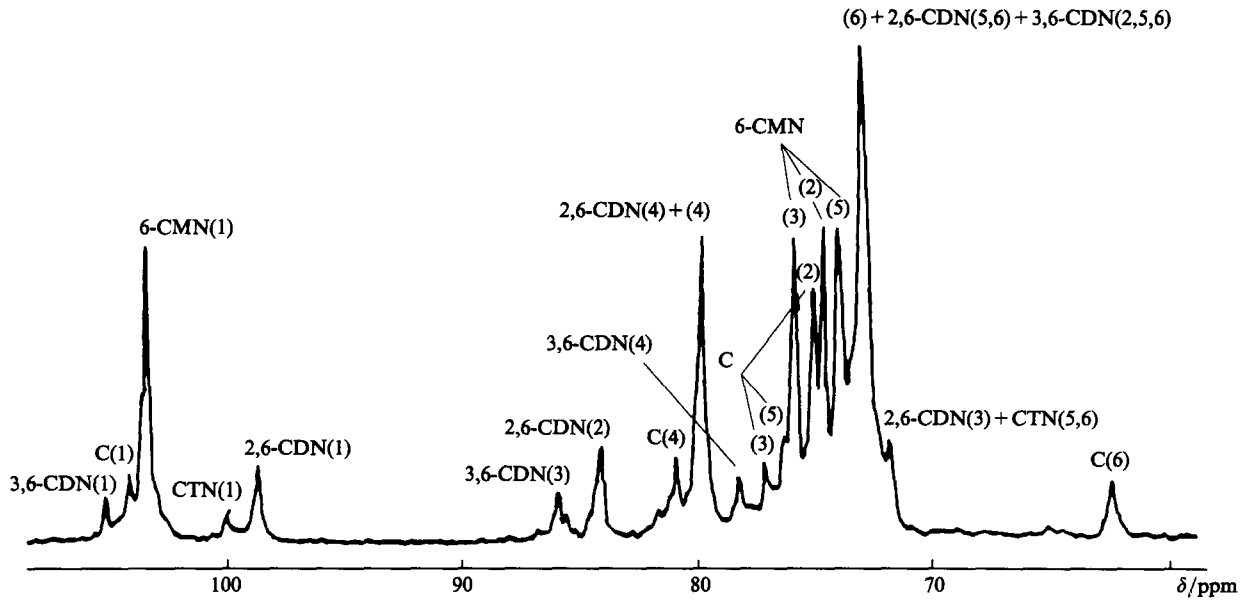


Figure 7. The ^{13}C NMR spectrum of a cellulose nitrate specimen with a degree of substitution of 1.2 in solution in DMSO showing the assignments of the signals to the corresponding units (the number of the ring carbon atom is indicated in brackets).[41]

The presence of the nitrate group in the 2-position is characterised by the presence of C(1) signals in the region of 100 ppm for any types of substitution in the remaining positions (see Table 4), whilst its absence leads to the displacement of the signals of the C(1) atom to the region of 104 ppm. Apparently this is a convenient analytical feature for the determination of the type of substitution. Analysis of the chemical shifts of the C(1) atom for model nitrates of methyl β-D-glucosides has confirmed the above conclusion that the conformational state of the cellulose nitrate chains influences significantly the positions of the signals in the NMR spectrum. Evidently the conformer most stable for the given solvent is formed in the model nitrates, this being indicated by the small differences between the maximum and minimum chemical shifts (Table 4). They also indicate that the C(1) nucleus is less 'sensitive' to the type of substitution in a small molecule than in a chain molecule and this is also evidence for the greater conformational freedom of the cellulose nitrate macromolecules. In order to detect more detailed effects (such as the influence of neighbours), it is necessary to increase significantly the resolution afforded by the spectrometer. For example, comparison of the spectra of the same cellulose nitrate specimen obtained on instruments with different working frequencies shows a marked increase in the complexity of the spectrum, which undoubtedly reflects the influence of secondary effects. However, the interpretation of such spectra still remains difficult.

Analysis of the NMR spectra demonstrated the similarity of the Overhauser effects and the spin–lattice relaxation times for all the carbon nuclei of the glucopyranose ring of cellulose nitrates, which had been indicated earlier by Wu[33] and Clark.[35] This agrees well with the fact that the charges on different oxygen atoms in glucose and its nitrates, obtained from quantum-chemical calculations, are similar.[46] Taking this into account, it is possible to carry out quantitative measurements of the partial degrees of substitution in the 2-, 3-, and 6-positions and also to find the fractions of units with different types of substitution in cellulose nitrates. A series of publications have appeared[33, 35–37, 40, 44, 47–54] whose authors measured the contents of the principal types of units in cellulose nitrates. It is noteworthy that the contents of 2-mono-, 3-mono-, and 2,3-di-nitrate units in cellulose nitrates are very low and for this reason they are usually not measured. (An exception is a study[44] where it was shown that the fractions of the above units are 0.039, 0.021, and 0.047 respectively.)

Progress in the study of the detailed structure of cellulose nitrates was achieved after high-resolution ^{13}C NMR spectra had been obtained in the solid state.[7, 8, 55–59] New results were obtained with the aid of this method, from which it was possible to trace the characteristic features of the formation of the cellulose nitrate matrix during the nitration of cellulose and, at the same time, to assess the conformational rearrangement of the macromolecules. A characteristic feature is that the transition of solutions to the solid phase of cellulose nitrates leads to appreciable downfield shifts and a significant broadening of the lines in the ^{13}C NMR spectra.[58] Thus the following values of δ were obtained for CTN:

C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
101.8	72.1	72.1	72.1	72.0	72.0

The main cause of the change in δ (cf. Table 3) may be, first, the loss of mobility by the chains and, second, the differences between the conformational states of the cellulose nitrate macromolecules in solution and in the bulk phase. The latter are characterised by a much more diverse set of conformations of the chains and substituents. For the C(1) nucleus in solutions of cellulose nitrates (Table 4) it is possible to differentiate two groups of signals for the cellulose nitrate unsubstituted, or substituted, in the 2-position: (1) from the unsubstituted unit and the 6-mono-, 3-mono-, and 3,6-di-substituted units; (2) from the 2-mono-, 2,3-di-, 2,6-di-, and 2,3,6-tri-substituted units. This subdivision can be readily detected also in the NMR spectra of the solid[58, 59] in the form of broad maxima in the regions of 105 and 100 ppm respectively. Evidently, with increase in the degree of substitution of the cellulose nitrate, the increase in the maximum at 100 ppm and the decrease in that at 105 ppm are associated with the increased content of the trinitrate units and the decrease in the fraction of the mono- and di-substituted and unsubstituted units. It is therefore wrong to attribute the changes in the intensities of these signals solely to the conformational rearrangement of the cellulose nitrate with increase in the degree of substitution during the course of nitration.[59]

We are aware of only two papers devoted to the study of high-resolution ^{15}N NMR spectra in solution.[42, 43] The principal signals of the nitrogen nuclei of the nitrate groups, occupying the 2-, 3-, and 6-positions, were assigned in both studies (Table 5).

Table 5. Positions of the signals (ppm) in the high-resolution ^{15}N NMR spectra of solutions of cellulose nitrates and model nitrates.

Position of the nitrate group	2,3,4,6-TNMG[43]	CON[43]		CN[43]	CN[42]
		A	*B*		
2	335.2	332.8	333.7[a]	335.5[b]	−1.0[c]
3	335.3	335.2	334.5	336.9	−2.4
6	340.6	339.6	340.1	341.1	3.2

[a] See Fig. 9.
[b] Degree of substitution 2.72, solution in acetone-d_6, external standard — $^{15}NH_4Cl$ + HCl. [c] Degree of substitution 2.35, solution in dimethyl sulfoxide, external standard — $H^{15}NO_3$.

As can be seen from the data presented, there are significant discrepancies in the interpretation of the signals from the N(2) and N(3) atoms. The reasons for these are so far obscure, but the authors[42] confirm the validity of their interpretation by showing that the relative intensities of the signals agree well with the partial degrees of substitution determined from the ^{13}C spectra. Nevertheless, a detailed analysis of the ^{15}N NMR spectra is lacking to date.

Proton magnetic resonance of cellulose nitrates yields much less information than ^{13}C NMR.[33,43] Systematic analysis of the ^{1}H, ^{13}C, and ^{15}N NMR spectra combined with the analysis of the NMR spectra of selectively substituted model saccharide nitrates will probably assist progress in studies on the detailed molecular structure of cellulose nitrates.

IV. Infrared spectroscopic study of the structure of cellulose nitrates

The vibrational spectroscopy of cellulose nitrates is almost fully represented by IR spectroscopic studies. The measurement of the Raman spectra of cellulose nitrates still constitutes a difficult experimental task.

The first IR spectrum of cellulose nitrate was recorded about 25 years ago.[5,15] Since then, there have been numerous publications devoted to the experimental study of the molecular structure of cellulose nitrates and their analogues by IR spectroscopy[6,7,11,14,44,60–77] and also to theoretical calculations of the vibrational spectra of the latter.[66,78,79] The low-frequency IR spectra of cellulose nitrates[64,68,70] and the nitrates of low-molecular-mass hydrocarbons[73] have been investigated particularly vigorously at the present time (undoubtedly as a result of the appearance of commercial FT-IR spectrometers). A detailed analysis of these spectra and also of the low-frequency spectroscopic characteristics of structural modifications of cellulose has been presented in another review[14] and will not therefore be considered here‡.

The IR spectroscopic data obtained by Watanabe et al.[15] and Panov and Zhbankov[5] were subsequently refined and supplemented by Kovalenko et al.[76] on the basis of the analysis of the IR spectra of cellulose nitrate enriched in ^{15}N and also of the polarised IR measurements for oriented cellulose nitrate fibres.

In the study of the region 2800–2950 cm^{-1} corresponding to absorption due to the $\nu(CH)$ and $\nu(CH_2)$ stretching vibrations of cellulose nitrates enriched in ^{15}N, it was observed for the first time that there is a Fermi resonance of the $\nu_a(CH_2)$ stretching vibration and of the $\nu_a(NO_2)$ + $\nu_s(NO_2)$ sum frequency. The observed redistribution of the intensities and the frequency shifts due to the Fermi resonance explain satisfactorily the dependence of the intensities of the absorption bands due to the CH and CH_2 groups in this spectral range on the degree of substitution of cellulose nitrate which had been discovered earlier.[11,60,71]

Analysis of the IR spectra of highly dilute solutions of cellulose nitrates in tetrahydrofuran (THF) in the range 1600–1700 cm^{-1}, where the $\nu_a(NO_2)$ stretching vibration of the nitrate groups is observed, indicates a doublet structure of the band[44,63,76] with 1662 and 1646 cm^{-1} components (Fig. 8); the first was assigned to the absorption by the nitrate groups occupying the 2- and/or 3-positions and the second was assigned to the absorption by the nitrate groups in the 6-position in the pyranose rings of cellulose nitrate.[44,76] The second derivatives of the spectrum in this range have been obtained[44] and a third high-frequency component of the band was detected. According to the authors, it is associated with the steric hindrance generated by the pair of neighbouring nitrate groups in the 2- and 3-positions in the pyranose ring of the cellulose nitrate. However, it follows from X-ray diffraction and calculated data[21–23,27,29,32] that such hindrance does not occur even in crystals of the model nitrates and it is therefore difficult to expect their appearance in dilute cellulose nitrate solutions. In their next study, the same workers[80] present the spectrum of the same cellulose nitrate specimen but this time without the third component. We emphasise that the doublet structure is readily manifested on an FT-IR spectrometer, with a resolution of 1 cm^{-1}, whereas on the usual dispersion instruments it had been previously impossible to observe it.[11,61]

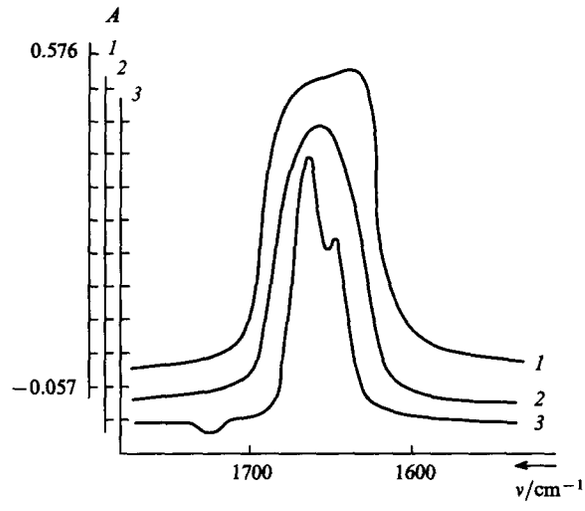


Figure 8. IR spectra of cellulose nitrate with a degree of substitution of 2.8. Specimen: (*1*) fibre; (*2*) film cast from an acetone solution; (*3*) dilute solution in THF.

A complex, diffuse contour of the $\nu_a(NO_2)$ band, the width of which reaches 90 cm^{-1}, can be observed in the IR spectra of fibrous and powdered cellulose nitrates (Fig. 8).[76,77] This width is due to the large set of conformational states of the chains and substituents. It has been suggested[11] that the extensive set of conformations can be accounted for by the inhomogeneity of the nitration of cellulose, where there is insufficient time for the chains to relax after the removal of the liquid phase and the conformations of the chains and the 'appendages' in cellulose nitrate are frozen. Comparison of the IR spectroscopic[77] and X-ray diffraction[82] data for the plasticisation of cellulose nitrates shows that the crystallinity of the cellulose nitrates does not contribute to the widening of the $\nu_a(NO_2)$ band; the narrowing of the band occurs before the plasticiser reaches the crystalline regions of the cellulose nitrate (Fig. 9). Consequently the conformational rearrangement of the chains accompanying their relaxation when the plasticiser is introduced leads to a decrease in

‡ We may note that the 516 and 490 cm^{-1} bands, which have a high dichroic ratio,[76] are due to the vibrations of the pyranose skeleton of the cellulose nitrate chain and are not associated with the vibrations of the trinitrate units as suggested in our earlier communication.[64]

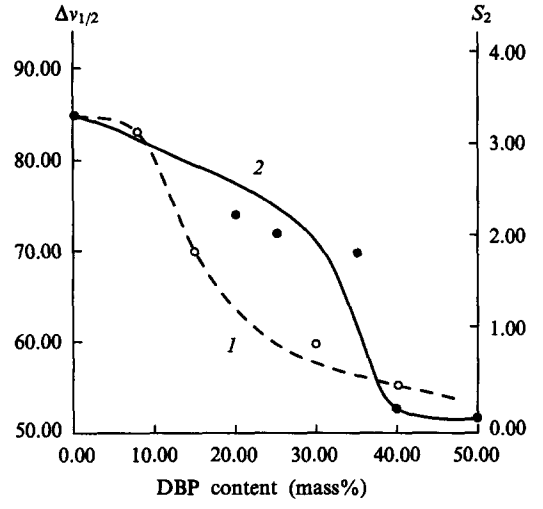


Figure 9. Dependence of the $\nu_a(NO_2)$ band width (curve *1*) in the IR spectra and of the crystallinity of cellulose nitrate S_2 (curve *2*) on the dibutyl phthalate content in the composition with cellulose nitrates.

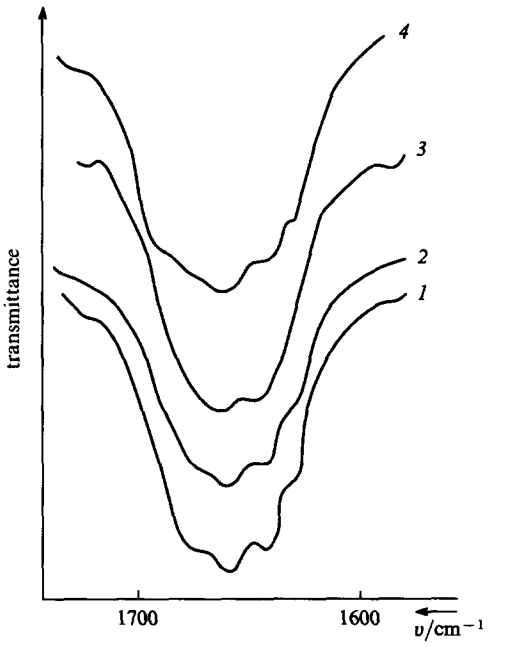


Figure 10. IR spectra of amorphous 2,3-DNMG (curve *1*), 2,3-DNMMG (curve *2*), 2,3,6-TNMMG (curve *3*), and 2,3,4,6-TNMG (curve *4*).

the diversity of the conformations of the nitrate groups and hence to a narrowing of the $\nu_a(NO_2)$ as well as the $\nu_s(NO_2)$ bands.[77]

Studies of the IR spectra of crystalline low-molecular-mass carbohydrate nitrates have been resorted to in the analysis of the complex contour of the $\nu_a(NO_2)$ band in the spectra of cellulose nitrates.[65–67,74] Unfortunately, in this case the transfer of the spectroscopic information obtained, which is itself extremely valuable, to cellulose nitrates is not always justified. Both the static field of the crystal and the Davydov (resonance) splitting are known to exert a significant influence on the position of the absorption band in the IR spectra of organic crystals. In all the crystalline nitrates of glucopyranosides investigated,[23–27] the primitive cell (which in this case is identical with the crystallographic cell) contains four molecules, and one must therefore expect four components due to the splitting of the band in the IR spectrum. Under these conditions, for example in the case of the 2,3,4,6-TNMG crystal, each molecule contains four nonequivalent nitrate groups: the primitive cell, which is in fact reflected in the IR spectrum, includes 16 spectroscopically nonequivalent nitrate groups. The contour of the $\nu_a(NO_2)$ band proves to be complex.[66,74] Effects characteristic of molecular crystals are virtually absent from cellulose nitrates as a consequence of the low crystallinity and defectiveness (owing to the heterounit structure) in the crystal packing of cellulose nitrates.[85] Incidentally, the picture is significantly different in the spectra of amorphous low-molecular-mass glucoside nitrates (Fig. 10): the triplet, doublet, and single $\nu_a(NO_2)$ bands observed in the spectra of 2,3,4,6-TNMG, 2,3-DNMMG, and 2,3-DNMG crystals are converted into bands which are now determined solely by the positions of the nitrate groups in the ring and by the conformational equilibrium in the molecules. For the same reason, it is necessary to treat with caution the application to cellulose nitrates data obtained for the $\nu_s(NO_2)$ band in the spectra of crystals of low-molecular-mass carbohydrate nitrates. In the cellulose nitrate spectrum, this band, like the $\nu_a(NO_2)$ band, is 'sensitive' to conformational rearrangements.[77]

The band due to the antisymmetric stretching vibrations of the nitrate groups in the cellulose nitrate spectra proved useful in determining the compositions of the elementary units[72] (in addition to ^{13}C NMR data): by measuring the ratio A_{1662}/A_{1648} of the optical densities of the components in the IR spectra of dilute cellulose nitrate solutions in THF, it is possible to estimate the ratio of different kinds of substituted cellulose nitrate units from the formula

$$\frac{A_{1662}}{A_{1648}} = \frac{[C_2] + [C_3] + 2\,[C_{23}] + [C_{26}] + [C_{36}] + 2\,[C_{236}]}{[C_6] + [C_{26}] + [C_{36}] + [C_{236}]}, \quad (1)$$

where $[C_{ijk}]$ is the fraction of units with a given type of substitution.

The ν(OH) stretching vibration bands are observed in the form of a broad band having a complex contour in the range 3300–3600 cm^{-1} in the IR spectra of cellulose nitrates with a degree of substitution less than three (Fig. 11). They are due to the hydroxy-groups of cellulose nitrate involved in the formation of hydrogen bonds. The most probable proton acceptors are the nitrate groups, the OH groups themselves, and the O(5) oxygen atoms of the pyranose rings. It has been shown[5–7,11,60–62] that the ~3570 cm^{-1} maximum is due to the hydroxy-groups involved in a weak hydrogen bond with the nitrate groups. At the same time, an absorption region with a maximum at 3430 cm^{-1} may be noted in the cellulose nitrate spectra (Fig. 11). It characterises the OH...OH type of intermolecular hydrogen bond and the O(3)H...O(5) intramolecular hydrogen bond in neighbouring glucopyranose rings.[86,87] Calculations by the method of molecular mechanics showed[19] that a hydrogen bond of the latter type occurs in cellulose mono- and di-nitrates and that the energies of the hydrogen bonds of both types

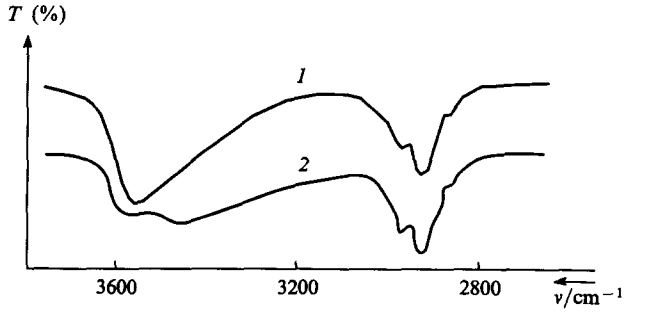


Figure 11. IR spectra of cellulose nitrates with a degree of substitution of 2.0 obtained by nitration in $HNO_3 + CH_2Cl_2$ (curve *1*) and $HNO_3 + H_2SO_4 + H_2O$ (curve *2*).

are similar §. As will be shown below, the ratio of the intensities of the ν(OH) bands at 3570 and 3430 cm^{-1} may be used to estimate the inhomogeneity in the mass distribution of the elementary units of cellulose nitrates.

V. Molecular spectroscopic study of the molecular-structural inhomogeneity of cellulose nitrates

The inhomogeneity in molecular-structure of cellulose nitrates with a degree of substitution less than three is associated with their heterounit structure and is determined by the inhomogeneity of the nitration process, where the final composition of the products depends significantly on the diffusional characteristics of the reaction system. In most cases, the initial cellulose and the final product (cellulose nitrate) are insoluble in the liquid reaction mass, and the morphological and fibrous structures of the initial cellulose are retained after nitration. By estimating the inhomogeneity of the cellulose nitrate with the given degree of substitution, it is possible to find a multiplicity of combinations of heterotypical units, which undoubtedly influence the properties of the cellulose nitrates. However, it has not previously been possible to estimate quantitatively the inhomogeneity of the cellulose nitrates. The methods based on the chemical or enzymic hydrolysis, which have been used successfully to determine the compositions of the elementary units of cellulose ethers, for example by Spurlin[88] and Reuben,[89] proved unsuitable for cellulose nitrates, since the elimination of the nitrate groups from the latter takes place significantly more readily than the dissociation of the glycosidic bonds.[90,91] For this reason, the determination of the composition of the elementary units and of the molecular-structural inhomogeneity of cellulose nitrates became possible only recently by virtue of the advances made in the study of the detailed molecular structures of cellulose nitrates by the high-resolution ^{13}C NMR and FT-IR spectroscopic methods.

1. Terminology

Since there is some terminological confusion in the literature on the molecular structure of cellulose esters, and the number of studies devoted to the inhomogeneity of such esters has been growing continuously, it has become necessary to define the terms used in the analysis of the molecular structure of cellulose esters — in this instance cellulose nitrates.

The degree of substitution γ is defined as the average number of substituting groups per glucopyranose ring in the cellulose nitrate macromolecule. The partial degree of substitution at the given carbon atom γ_i is the average number of substituting groups occupying the given position C_i. Clearly for cellulose nitrates we have

$$\gamma = \gamma_2 + \gamma_3 + \gamma_6.$$

For example, in the fully substituted CTN with a degree of substitution $\gamma = 3$, we have

$$\gamma_2 = \gamma_3 = \gamma_6 = 1.$$

The composition of the elementary units is expressed in fractions of unity and is defined by the relations[88]

$$s_0 + s_2 + s_3 + s_6 + s_{23} + s_{26} + s_{36} + s_{236} = 1,$$

where s_{ijk} is the fraction of units with the given type of substitution, and

$$c_0 + c_1 + c_2 + c_3 = 1,$$

where c_i are the fractions of unsubstituted and mono-, di-, and trisubstituted cellulose nitrate units. Evidently $c_0 = s_0$ and

$$c_1 = s_2 + s_3 + s_6,$$

$$c_2 = s_{23} + s_{26} + s_{36},$$

$$c_3 = s_{236}.$$

Here one may speak of six hypothetical cellulose nitrate homopolymers (cellulose 2-, 3-, and 6-mononitrates and 2,3-, 2,6-, and 3,6-dinitrates). The seventh homopolymer (CTN) does actually exist.

In the general case, the cellulose nitrate macromolecule represents an assembly of elementary units of eight types and an analogy with copolymers is appropriate here: statistical, block, etc.

2. Distribution of the units along the chain

The distribution of heterotypical units along the chain is also referred to as the microstructure or configuration of the chain.[92] By analogy with biopolymers, one may assume that each heterotypical cellulose nitrate unit represents a letter of the alphabet, so that the cellulose nitrate chain constitutes an eight letter 'word'. Unfortunately the current level of experimental technique does not permit the decoding of these cellulose nitrate 'words'. However, it is possible, in principle, to solve the problem of the frequency of the appearance of particular combinations of 'letters' for different methods of synthesis of cellulose nitrates. This problem has not yet been solved although the first attempts have already been made.[36,53]

3. Distribution of units in the bulk phase (in the matrix)

For the statistical distribution of the elementary units along the cellulose nitrate chain, one may expect that their distribution in the matrix is also statistical or homogeneous. The extreme case is the block character of the distribution of units along the chain. There is then a possibility of the aggregation of blocks of isotypical units into domains — three-dimensional regions of the cellulose nitrate matrix containing mainly chain fragments consisting of isotypical units. As a result of the inhomogeneous nature of the nitration of cellulose, a state intermediate between the cases quoted above occurs in the cellulose nitrate obtained.

The possibility of determining or estimating the composition of the elementary units, and of determining their distribution along the chain or in the bulk of the cellulose nitrate, gives rise to ways of analysing the inhomogeneity of cellulose nitrates, which is necessary both for the study of the mechanism and kinetics of the nitration of cellulose and for the preparation and processing of industrial cellulose nitrates.

4. Levels of inhomogeneity of cellulose nitrates

The molecular-structural inhomogeneity of cellulose nitrates is determined by a complex set of parameters: the composition of the nitrating mixture, the morphological structure of the initial cellulose determined by its origin (cotton, wood, linen, etc. celluloses), the conditions in the preparation of cellulose for nitration (activations of different kinds), and the nitration regimes. Naturally, without a logically well-founded subdivision in terms of the levels of inhomogeneity of cellulose nitrates, analysis of their properties becomes virtually impossible. For this reason, it has been suggested that their molecular-structural inhomogeneity be divided into several hierarchical levels:[72] in terms of the composition of the elementary units (compositional inhomogeneity); in terms of the distribution of heterotypical elementary units along the chain (configurational inhomogeneity); and in terms of the distribution of heterotypical elementary units in the cellulose nitrate matrix (matrix inhomogeneity).

5. Inhomogeneity of cellulose nitrates in terms of the composition of the elementary units

The compositions of the elementary units of cellulose nitrates[33,35,36,44,48–54] and of a number of other polysaccharide derivatives[93–96] have now been quite reliably determined by

§ O K Nugmanov. Personal communication.

high-resolution ^{13}C NMR in solution. Systematic analysis of the inhomogeneity at this level is only possible when a single methodological approach, permitting a comparison of data obtained for different nitrating mixtures, initial celluloses, etc., is employed. Attempts to achieve such an approach have been undertaken,[36,97] but, in our view, they have not been successful, because the criteria employed were not clearly defined and there were no 'reference points' for the inhomogeneity of the cellulose nitrates. A simple scheme for the determination of the inhomogeneity of cellulose nitrates in terms of the composition of elementary units (suitable, incidentally, for any derivatives of cellulose and of polysaccharides in general) has been proposed.[86] The concepts of cellulose nitrates with limiting homogeneity and limiting inhomogeneity were introduced in the above study. Cellulose nitrates with integral degrees of substitution are assumed to have the limiting homogeneity: 1 — cellulose mononitrate, 2 — cellulose dinitrate, and 3 — cellulose trinitrate. Here no account is taken of the specific positions of the nitrate groups in the elementary unit. For degrees of substitution of 1.2 and 2.5, cellulose nitrates containing respectively 20% of disubstituted and 80% of monosubstituted units, and 50% of dinitrate and trinitrate units, are considered to be homogeneous to the limiting extent. Cellulose nitrates consisting only of trinitrates and unsubstituted units are considered to have the limiting inhomogeneity.

In order to measure the inhomogeneity of cellulose nitrates in terms of the composition of the units, one determines the sum of the deviations, $\Sigma\Delta_i$, of units of the given type (tri-, di-, and monosubstituted as well as unsubstituted) from cellulose nitrates homogeneous to the limiting extent and with the same degree of substitution:

$$\Delta_i = |a_i - a_i^0|,$$

where a_i and a_i^0 are the measured and calculated fractions of the ith type units respectively. Analogous calculations are performed for the hypothetical cellulose nitrates which are inhomogeneous to the limiting extent, whereupon the dependence of $\Sigma\Delta_i$ on the degree of substitution of the cellulose nitrate is represented graphically by the 'inhomogeneity trapezium' (Fig. 12), the base of which is the cellulose nitrate homogeneous to the limiting extent in terms of the composition of the elementary units ($\Sigma\Delta_i = 0$), while the other three sides bound the region of existence of cellulose nitrates with any homogeneity (with respect to the composition of the units).

Models of the esterification of cellulose have been analysed[88] in terms of the quasi-homogeneous approximation (with thermodynamic and kinetic monitoring of the reaction products) and calculations have been made of the fractions of the unsubstituted, monosubstituted, disubstituted, and trisubstituted units in accordance with the constants for the substitution of the hydroxy-groups in the 2-, 3-, and 6-positions in the glucopyranose rings. These were subsequently revised for cellulose nitrates.[33,40,97] The values of $\Sigma\Delta_i$ were calculated from these data and plotted (Fig. 12). The figure includes also all the available experimental data for cellulose nitrates. The inhomogeneity with respect to composition of elementary units is determined by the distance from the abscissa axis of the values of $\Sigma\Delta_i$ calculated from the experimental measurements. The cellulose nitrates obtained by nitration in mixtures of nitric and sulfuric acids and in solutions of nitrogen oxides in nitric acid, as well as denitrated cellulose nitrates, proved to be the most inhomogeneous. These results will be examined in detail in the next section. Here we may note the clarity of the proposed procedure and the possibility of comparing polysaccharide derivatives with any compositions of the elementary units. For example, in the selectively substituted cellulose 2,3-diacetate (degree of substitution 1.69), the compositional inhomogeneity is very low and $\Sigma\Delta_i = 0.18$.[93] Carboxymethylcellulose with a low degree of substitution (0.7) has $\Sigma\Delta = 0$,[94] whilst a cellulose ether (degree of substitution 1.27) also exhibits a high inhomogeneity

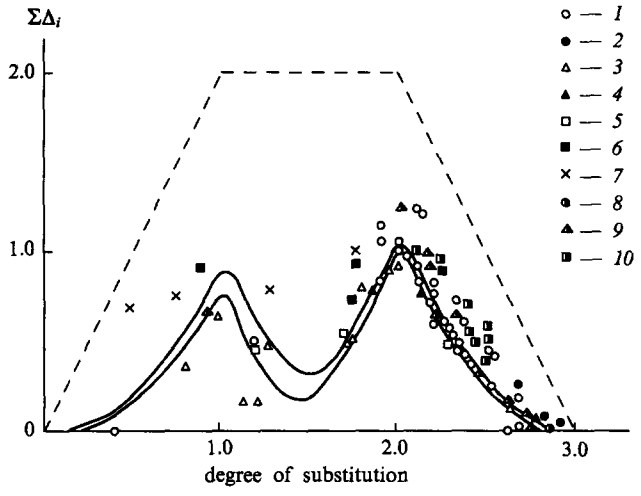


Figure 12. The sums of the deviations $\Sigma\Delta_i$, measured by ^{13}C NMR, of the compositions of the elementary units of cellulose nitrates obtained by nitration in the $HNO_3+H_2SO_4+H_2O$ [33,36,40,44,48–50,53] (curve *1*), $HNO_3+H_2SO_4$ [49] (curve *2*), HNO_3+H_2O [50,53,54] (curve *3*), and $HNO_3+CH_2Cl_2$ [40] (curve *4*) mixtures, in HNO_3 vapour [50,53,54] (curve *5*), in the $HNO_3+N_2O_5$ [50] (curve *6*), $HNO_3+N_2O_5+N_2O_4$ (Yu M Kargin, personal communication) (curve *7*), and $HNO_3+H_3PO_4+P_2O_5$ [35] (curve *8*) mixtures, and by denitration in the HNO_3+H_2O [35,50,53] (curve *9*) and $HNO_3+H_2SO_4+H_2O$ [48] (curve *10*) mixtures. Calculated sums of the deviations $\Sigma\Delta_i$: continuous curves — according to Spurlin:[88] upper curve — for the equilibrium constant ratios $K_6 : K_2 : K_3 = 10 : 1 : 1$, lower curve — for the rate constant ratios $k_6 : k_2 : k_3 = 10 : 1 : 1$; dashed line — calculated sums of the deviations $\Sigma\Delta_i$ for cellulose nitrates with the limiting inhomogeneity.

with respect to the composition of the elementary units with $\Sigma\Delta_i = 0.36$.[95] It is of interest that the amylose nitrates obtained by inhomogeneous nitration and having degrees of substitution of 1.69 and 2.17 are characterised by $\Sigma\Delta_i = 0.68$,[96] which is close to the value calculated by Spurlin's method (Fig. 12), whereas the homogeneously denitrated amylose nitrate with a degree of substitution of 1.89 has $\Sigma\Delta_i = 0.08$.

The limitation of the applicability of high-resolution NMR to polymer solutions should be noted. Only the dissolved part of the polymer contributes to the signal intensities, and for low degrees of substitution the solubility of cellulose nitrates in organic solvents is low. This is in fact the reason why the limiting homogeneity of the cellulose nitrate specimen with a degree of substitution of 0.4, found by Wu,[33] is a 'consequence' of neglecting this limitation.

Results obtained by IR spectroscopy may be used to estimate the inhomogeneity from the ratio of the optical densities of the 1662 and 1648 cm^{-1} bands by using Eqn (1). Unfortunately, this method too, which is simpler than the NMR procedure, suffers from a disadvantage — no account is taken of the unsubstituted units, i.e. the applicability of the method is limited to the region where the degree of substitution is greater than two, in which the fraction of these units becomes negligible.

6. Distribution of elementary units along the cellulose nitrate chain

Currently, the distribution of the elementary units along the cellulose nitrate chain is not susceptible to direct measurement, although it is possible in principle. Such distribution can, however, be inferred indirectly from combined data on the compositional and matrix inhomogeneities of cellulose nitrates. We may note that both the compositional and the configurational inhomogeneities of cellulose nitrates are characteristics of macromolecules; account must be taken of the fact that all the data presented here are estimates of both levels of

inhomogeneity, averaged over the entire assembly of macromolecules. If it is necessary to investigate the compositional inhomogeneity of the macromolecules themselves, one has to resort to methods developed for the investigation of the molecular-mass distribution of cellulose nitrates—for example fractionation, gel-permeation chromatography with different detection procedures, etc.

7. Distribution of heterotypical units in the cellulose nitrate matrix

The distribution of heterotypical units in the cellulose nitrate matrix has been investigated very fully. Most of the results have been obtained by X-ray photoelectron spectroscopy (XPS). This method yields information about the elementary composition of the material on the surface to a depth of the order of tens of nanometers.[8] By comparing the contents of nitrate groups on the surfaces of cellulose nitrate fibres, measured by the XPS method, and in the bulk of the material, it is possible to infer the matrix inhomogeneity of the cellulose nitrate. It has been shown[98] that nitration of cellulose by the $HNO_3 + H_3PO_4 + P_2O_5$ and $HNO_3 + P_2O_5 + H_2O$ mixtures proceeds uniformly on the surface and in the bulk of the fibres, attaining simultaneously identical degrees of substitution, whereas in nitration by the $HNO_3 + H_2SO_4 + H_2O$ mixtures the final degree of substitution is attained rapidly on the surfaces of the fibres but, even after nitration for 2 h, the degree of substitution within the fibres remains smaller than on the surface. Nitration of cellulose by a solution of the nitronium salt $NO_2^+BF_4^-$ in general takes place only on the surfaces of the cellulose fibres without involving the inner region.[99]

The results of X-ray phase analysis (XPA) have shown that the crystal structure of cellulose nitrate is already formed during the nitration process. In the nitration of cellulose by $HNO_3 + H_2SO_4 + H_2O$ mixtures, the reflections due to the nonnitrated regions of the cellulose are still observed, together with the reflections due to crystalline cellulose nitrates, even for a degree of substitution of 2.[100–103] Furthermore, on raising the water content in the above mixture from 0% to 15%, it was observed[52] that the inhomogeneity of the resulting cellulose nitrates diminished: the reflections due to crystalline cellulose vanish at lower degrees of substitution, while the formation of cellulose nitrate crystallites begins at higher degrees of substitution. Nitration of cellulose with the $HNO_3 + CH_2Cl_2$ mixture is characterised by the formation of a more homogeneous cellulose nitrate structure: the reflections due to cellulose have already disappeared for a degree of substitution of 0.1, whereas the crystallinity of the cellulose nitrates begins to be manifested only for a degree of substitution > 1.2.[102,104] It has also been shown by the XPA method that the products of the nitration of cellulose of different origins (cotton and wood celluloses) in the same nitrating mixture are different, the most homogeneous cellulose nitrates being obtained when cotton cellulose is employed.[103] The data obtained by high-resolution ^{13}C NMR in the solid state lead to similar conclusions.[10,105] Seemingly, by employing the XPA method for the analysis of the dynamics of the cellulose nitration process as a function of time, it is possible to discover the characteristics of the establishment of the inhomogeneity of the cellulose nitrates: the lower the degree of substitution at which the reflections due to crystalline cellulose vanish and the higher the degree of substitution at which the crystal packing of cellulose nitrate begins to be established, the more homogeneous is the cellulose nitrate obtained.

The establishment of the inhomogeneity of cellulose nitrates has been analysed by IR spectroscopy for two nitrating media—concentrated HNO_3 and the $HNO_3 + H_2SO_4 + H_2O$ mixture.[106] The ratios of the cellulose nitrate fractions soluble and insoluble in acetone were determined in samples taken during the nitration process, and the degrees of substitution of both fractions were found for each specimen from the formulae

$$\gamma_s = 3 - \frac{3-\gamma}{a_s(1 + a_u b_u/a_s b_s)}, \text{ and } \gamma_u = 3 - \frac{3-\gamma}{a_u(1 + a_s b_s/a_u b_u)},$$

where γ is the degree of substitution of the given cellulose nitrate specimen, γ_s and γ_u are the partial degrees of substitution, a_s and a_u are the mole fractions, and b_s and b_u are the relative optical densities of the ν(OH) bands due to the hydroxy-groups in the soluble (s) and insoluble (u) fractions of the cellulose nitrate respectively (Table 6). In order to estimate the inhomogeneity of the cellulose nitrate, the deviations of the partial degrees of substitution from the overall degree of substitution were calculated from the relations

$$\Delta_s = \frac{\gamma_s - \gamma}{\gamma}, \quad \text{and} \quad \Delta_u = \frac{\gamma - \gamma_u}{\gamma}.$$

Evidently the smaller the values of Δ_s and Δ_u, i.e. the closer the partial and overall degrees of substitution of cellulose nitrates, the greater the homogeneity of the latter. In the course of the nitration by the ternary mixture, the degrees of substitution of the

Table 6. Partial degrees of substitution of cellulose nitrate fractions soluble and insoluble in acetone.

γ	$10^{-2}\tau$/s		ρ (mass %)		γ_s		γ_u		Δ_s		Δ_u	
	I	II	I	II	I	II	I	II	I	II	I	II
1.2	–	0.15	–	55	–	1.9	–	0.6	–	0.58	–	0.50
1.4	–	0.25	–	61	–	2.0	–	0.7	–	0.42	–	0.50
1.4	–	0.30	–	61	–	1.9	–	0.8	–	0.57	–	0.43
1.5	–	0.60	–	68	–	2.0	–	0.7	–	0.47	–	0.53
1.7	0.15	–	68	–	1.9	–	1.3	–	0.12	–	0.24	–
1.8	0.20	–	67	–	2.0	–	1.4	–	0.11	–	0.24	–
1.9	–	1.8	–	83	–	2.2	–	0.8	–	0.16	–	0.58
2.0	0.25	–	69	–	2.2	–	1.6	–	0.10	–	0.20	–
2.2	0.30	–	76	–	2.4	–	1.7	–	0.09	–	0.23	–
2.3	–	7.8	–	99	–	2.3						
2.3	–	18	–	100	–	2.3						
2.5	1.8	36	100	100	2.5	2.5						
2.7	7.8	–	100	–	2.7	–						
2.7	18	–	100	–	2.7	–						
2.7	36	–	100	–	2.7	–						

Note. The following notation has been adopted: τ = nitration time; ρ = solubility; nitrating mixtures: I—98% HNO_3; II—39% HNO_3 + 56% H_2SO_4 + 5% H_2O.

fractions soluble and insoluble in acetone differ significantly from the degree of substitution of the specimen analysed, so that the inhomogeneity of the latter is appreciably greater than that of the cellulose nitrate obtained by nitrating cellulose with concentrated nitric acid.

The residual hydroxy-groups present in the elementary cellulose nitrate units (with the exception of the fully substituted ones) are a kind of label. They can form hydrogen bonds of different types in the cellulose nitrate matrix. Taking this into account, the distribution of the labels in the bulk of the cellulose nitrate has been estimated quantitatively.[86] Those cellulose nitrates in which there is a statistical distribution of the heterotypical units in the bulk phase are matrix-homogeneous. We therefore calculated[86,87] the ratio of the probabilities of the formation of weak hydrogen bonds between the hydroxy- and nitrate groups, of strong hydrogen bonds of the type OH...OH, and of intramolecular hydrogen bonds of the type OH(3)...O(5) from only the degree of substitution of the cellulose nitrates by means of the formula

$$P_r = k\frac{\gamma}{3-\gamma},$$

where k is a coefficient which takes into account the fraction of the intramolecular hydrogen bonds. The ratios A_{3570}/A_{3440}, reflecting the actual ratios of the different types of hydrogen bonds involving the residual OH groups in the cellulose nitrate and determined experimentally from the IR spectra, were used to plot the $P_r = f(\gamma)$ relation (Fig. 13). The relation between this level of inhomogeneity, determined by a somewhat different method, and the thermal stability of the cellulose nitrates has been demonstrated.[107]

We may note that there is complete agreement between the results of the measurements of both levels of inhomogeneity — compositional (Fig. 12) and matrix (Fig. 13) inhomogeneities. This evidently reflects their hierarchical relation because nitration in all the nitrating media examined above takes place inhomogeneously. It is quite likely that the use of nontraditional nitration methods, for example transesterification under homogeneous conditions or the application of new selectively substituting reagents, will lead to inconsistent data for different levels of inhomogeneity.

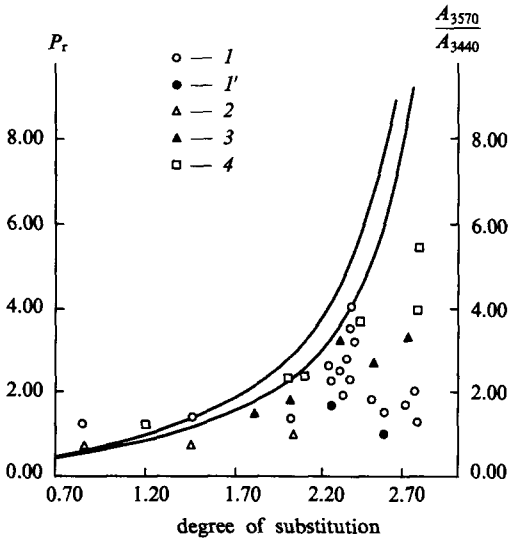


Figure 13. Deviations of the optical densities (A_{3570}/A_{3440}) of cellulose nitrates obtained by nitration in $HNO_3 + H_2SO_4 + H_2O$ (*1*, *1'*), $HNO_3 + H_2SO_4$ (*2*), $HNO_3 + H_2O$ (*3*), and $HNO_3 + CH_2Cl_2$ (*4*) mixtures. (*1'*) cellulose nitrate films cast from solutions in acetone; the P_r curves have been calculated for two values of k.[86]

VI. Inhomogeneity of the nitration and inhomogeneity of cellulose nitrates

Cellulose nitrates obtained by nitration with $HNO_3 + H_2SO_4$, $HNO_3 + H_2SO_4 + H_2O$, $HNO_3 + N_2O_5$, and $HNO_3 + N_2O_5 + N_2O_4$ mixtures, as well as the denitrated cellulose nitrates, are most inhomogeneous in terms of the composition of the elementary units and in the matrix. More homogeneous cellulose nitrates have been synthesised in liquid and gaseous nitric acid, in its aqueous solutions, and in nitric acid–dichloromethane mixtures. It was found that such subdivision in terms of inhomogeneity correlates satisfactorily with the presence or absence of nitronium ions NO_2^+ in the initial nitrating mixtures. Thus, in a mixture of sulfuric and nitric acids, the latter is dissociated to a considerable extent[108–111] with formation of the most inhomogeneous cellulose nitrates (Fig. 12). The addition of water to this mixture of acids lowers the NO_2^+ concentration[109,111] and the inhomogeneity of the cellulose nitrates in terms both of the composition of the elementary units and of the matrix (Fig. 13). Nitration with a solution of the nitronium tetrafluoroborate salt[99] leads to the formation of a surface layer of cellulose nitrates on nonnitrated cellulose fibres. The mixture of nitric acid with N_2O_5 is also characterised by a high concentration of nitronium ions.[112,113]

The content of nitronium ions in aqueous solutions of nitric acid with a HNO_3 concentration in excess of 80% is low;[114] the degree of ionisation of the acid varies within the limit of 0.03. The compositional inhomogeneity does not then exceed the values calculated by Spurlin's method and the matrix inhomogeneity of the cellulose nitrates obtained in 98% nitric acid is significantly lower than that of the cellulose nitrates synthesised in the $HNO_3 + H_2SO_4 + H_2O$ mixture (Table 6, Fig. 13). Nitronium ions have not been detected in the $HNO_3 + CH_2Cl_2$ mixtures,[115] which has been confirmed by studies on the Raman spectra of this mixture in the nitric acid concentration range from 30% to 80%. Cellulose nitrates obtained by nitration in this mixture are the most homogeneous (Figs 12 and 13).

Several points of view on the mechanism of the nitration of cellulose exist at the present time. The elementary step in the reaction reduces mainly to the $Cell-OH + NO_2^+$, $Cell-OH_2^+ + HONO_2$, and $Cell-OH_2^+ + N_2O_5$ interactions or their combinations.

In order to elucidate the relation between the inhomogeneity of the cellulose nitrate obtained and the presence of nitronium ions in the initial acid mixture, we shall consider the following scheme: the elementary step of the reaction requires an active pair consisting of the nitronium ion and a hydroxy-group of cellulose, the molecular form of nitric acid or N_2O_5, and the protonated form of the hydroxy-groups of cellulose. In this case, the nitration of cellulose must be regarded as the combination of three proceses occurring simultaneously:

(1) diffusion of the nitrating mixture to the polymer matrix;
(2) the formation of the active pairs;
(3) the interaction of the active pairs (nitration proper).

These processes are followed by the counterdiffusion of the species (molecules and ions) comprising the nitrating mixture and the low-molecular-mass reaction product in microregions of the matrix of the cellulose being nitrated. Since the rate of nitration (process 3) is significantly higher than the rates of the first two processes, the homogeneity of the cellulose nitrates obtained depends on the ratio of the rates of processes 1 and 2.

If the nitrating mixture contains initially the nitronium ions NO_2^+, i.e. both components of the active pair are already present in the reaction mass, process 2 is ruled out and the reaction proceeds topochemically (Fig. 14, curve *1*). The rate of this reaction is limited by the diffusion of nitronium ions into the cellulose matrix, and leads to the formation of an inhomogeneous cellulose nitrate. On the other hand, if process 2 plays a significant role, then the active pairs interact at the site of the increase in their concentration and, what is most important,

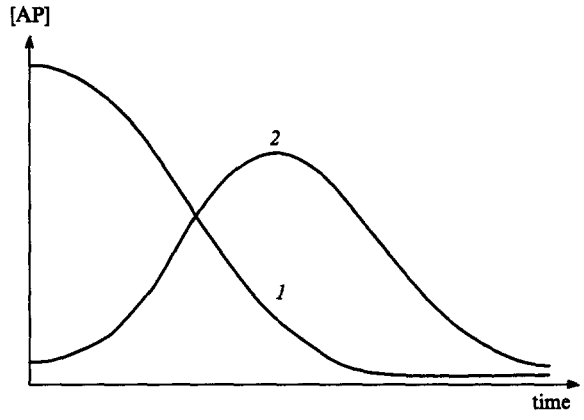


Figure 14. Variation of the concentration of the active pairs [AP] during the diffusion of the nitrating mixture into the cellulose matrix: (*1*) in the presence of both components of the pair at the beginning of nitration; (*2*) on formation of the active pairs during nitration.

under the conditions of a more or less uniform distribution resulting from the diffusion of the nitrating mixture (process 1) into the cellulose matrix (Fig. 14, curve *2*). The reaction then proceeds quasi-homogeneously and a more homogeneous cellulose nitrate is therefore formed. There is no doubt that the real nitration pattern is the average of those illustrated in Fig. 14. The rate of diffusion can evidently vary depending on the ability of the nitrating mixture to 'loosen' the cellulose matrix, but the formation of active pairs probably plays the main role in the establishment of the inhomogeneity.

The products of the denitration of cellulose nitrates obtained by treating the latter with solutions of nitric acid[35,50,53] or the sulfuric acid–nitric acid mixture[48] have the most inhomogeneous elementary units. Seemingly the denitration of cellulose nitrates has different features as regards both the mechanism[116] and the diffusional characteristics. Experimental data (XPA) have shown[36,48] that the denitration involves the cellulose nitrate crystallites to only a slight extent, the diffusion of the denitrating mixture in the latter being significantly limited. For this reason, the denitration proceeds mainly in the nonordered sections of the cellulose nitrate matrix, whereupon a considerable proportion of the dinitrate and trinitrate units, which constitute the bulk of the cellulose nitrate crystallites, are retained and the inhomogeneity of the denitrated cellulose nitrates increases. This has been confirmed by the finding that the last point for the denitration of cellulose nitrates by the acid mixture, corresponding to a degree of substitution of 2.1 (over a period of 7 days) (Fig. 12), fits on the calculated curve. The inhomogeneity of this cellulose nitrate is significantly lower, which can be accounted for by the disruption of the morphological structure,[48] the degradation of the specimen, and hence a sharp increase in the accessibility of the bulk of the cellulose nitrate to the denitrating agent.

Thus, by monitoring the molecular-structural inhomogeneity of cellulose nitrates, it will evidently be possible to estimate directly the role of the diffusional component in the analysis of the kinetics of the inhomogeneous cellulose nitration reaction.

VII. Conclusion

The inhomogeneity of the nitration of cellulose affects significantly the properties of the resulting cellulose nitrates directly via their molecular-structural inhomogeneity. In the synthesis of new cellulose nitrate materials with more stringent requirements as regards homogeneity (for example biological membranes, detectors of ionising radiations, enamels, varnishes, etc.), it becomes possible to alter in a planned manner the conditions in the synthesis by taking into account the results of the analysis of the inhomogeneity of the cellulose nitrates obtained. The molecular-structural inhomogeneity must also be monitored when new selective reagents are used in the nitration of cellulose and in carrying out homogeneous transesterification or nucleophilic substitution reactions, whereupon it is possible to increase the selectivity of substitution in specific positions in the glucopyranose ring; the latter factor makes it possible to obtain new cellulose derivatives which cannot be synthesised directly from cellulose itself.

The theoretical ideas concerning the kinetics of macromolecular reactions have been mainly developed for homogeneous conditions[92,117–119] and all investigators agree unanimously that the development of approaches to the description of the kinetics of heterogeneous reactions closest to the real technological processes is an extremely complex task. The studies in the field of the kinetics of inhomogeneous processes, vigorously prosecuted in recent years,[120] involve the reactions of polymers.[120,121] The creation of models of this kind requires a detailed analysis of the changes in the structures of the reaction products, analogous to that proposed for the cellulose nitration reactions.

The applicability of the approaches developed for the analysis of the molecular-structural inhomogeneity of cellulose nitrates to other cellulose derivatives must be pointed out yet again. This applies primarily to the acetates and ethers for which adequate NMR and IR spectroscopic data are at present available.

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